

Arene hydrogenation by homogeneous catalysts: fact or fiction?

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Received 24th March 2003, Accepted 23rd April 2003
First published as an Advance Article on the web 20th May 2003

A few years ago the concept of homogeneous arene hydrogenation catalysis was called into question, since many catalysts originally assigned as homogeneous have subsequently been shown to be precursors to heterogeneous (colloidal or nanoparticulate) catalysts. In this Perspective, the mechanism for arene hydrogenation is described and extended to include polynuclear (cluster, colloidal and nanoparticulate) catalysts. The various experiments used to determine whether catalysis is by homogeneous or heterogeneous species are then assessed. The current catalysts in the literature are categorised, including those able to bring about partial reduction of aromatic compounds. Finally, the role of the solvent, including ionic liquids, is described, as the solvent could prove to be crucial in stabilising one form of catalyst over the other and in providing regioselective hydrogenation.

Introduction

Arene hydrogenation catalysis is a fascinating area of research in which many highly innovative and imaginative systems have been developed. Although much of the work has been curiosity driven, the reduction of arenes is an important reaction, with applications ranging from small scale synthesis¹ to industrial processes, for example, the synthesis of cyclohexane (a precursor to adipic acid used to produce nylon)² and other

reactions used in the oil industry³ and in paper production.⁴ Although it is not envisaged that homogeneous arene hydrogenation catalysts will replace heterogeneous catalysts in large scale industrial processes, the use of selective homogeneous arene hydrogenation catalysts in the synthesis of fine chemicals can be envisaged, because many substituted arenes are readily available and the most convenient route to a cyclohexyl analogue would be *via* hydrogenation. In principle, there is considerable potential for the simplification of many multi-stage synthetic procedures and the use of alternative precursors, should suitable catalysts become available.

The greater number of arene hydrogenation catalysts are based on the platinum group metals, and while the majority are heterogeneous, it is conceivable that all the so-called homogeneous catalysts are actually precursors to heterogeneous catalysts. Typically, heterogeneous catalysts comprise metals supported on fixed beds, generally operated under harsh conditions,⁵ or metal colloids and nanoparticles, which can be used under milder conditions.⁶ A number of molecular compounds have been reported to homogeneously catalyse the hydrogenation of arenes, although many have since been shown to be precursors to heterogeneous catalysts. The re-examination of one well-known catalyst led to the conclusion that the active catalysis was actually colloidal, leading the authors to question the whole concept of homogeneous arene hydrogenation catalysis.⁷ Recently, an excellent review that describes colloidal arene hydrogenation catalysis⁸ has appeared, and a more general review on colloidal catalysis⁹ places the former firmly in context. Compared to many of the apparently homogeneous catalysts that have been reported, these colloids operate under much milder conditions and are often slightly more active, conflicting with the general perception that homogeneous catalysts are more active than heterogeneous catalysts under ambient conditions. In this article, the supposed homogeneous catalysts are examined and evidence presented to suggest that the problem of ascertaining whether a catalyst is homogeneous or heterogeneous could be exacerbated by the choice of solvent.

In 2002, Paul Dyson became the Director of the Laboratory of Organometallic Chemistry at the Swiss Federal Institute of Technology in Lausanne (EPFL). His research is focussed on the catalytic and biological applications of organometallic compounds. He commenced a PhD in transition metal cluster chemistry at the University of Cambridge under the supervision of Prof. Brian F. G. Johnson and moved with the group to the University of Edinburgh, where he completed his PhD. After a one year post-doctoral fellowship, he took up a fixed-term lectureship at Imperial College of Science, Technology and Medicine. He became a Royal Society University Research Fellow in 1995 and transferred to the University of York in 1998, before moving to his current position.

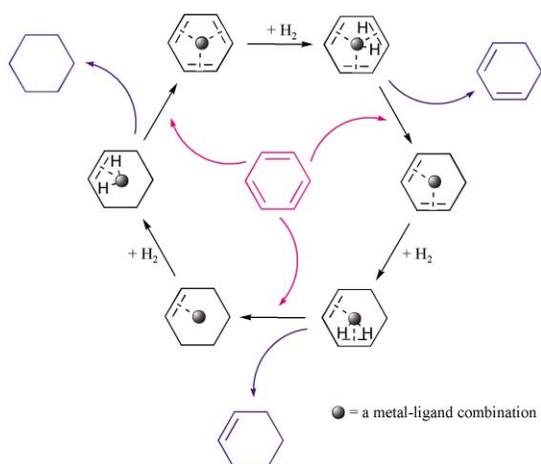


Paul J. Dyson

The arene-exchange mechanism

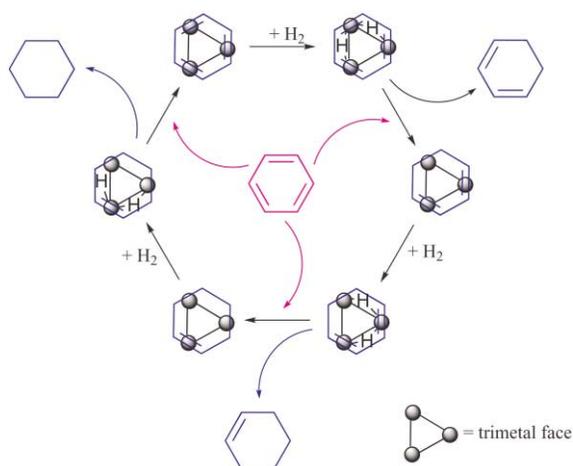
The generally accepted mechanism for the hydrogenation of arenes was proposed in 1974.¹⁰ The mechanism extrapolates from the observation that labile arene exchange takes place in a number of metal-arene complexes¹¹ and the so-called 'arene-exchange mechanism' is illustrated in Scheme 1.

It should be noted that there is no evidence to suggest that the point of association of fresh substrate is connected to the loss of the various hydrogenation products; however, the metal centre could become highly unsaturated unless a donor solvent coordinates or an incoming arene substrate starts to 'slip on' as the outgoing hydrogenated arene 'slips off'. Analogues of all the intermediate arene (η^6), cyclohexadiene (η^4) and cyclohexene (η^2) bonding modes shown in the Scheme have been crystallographically characterised.¹² Such structural data typically represent the first step in the experimental elucidation of the catalytic cycle, but direct experimental data for this reaction have not been forthcoming.



Scheme 1 An interpretation of the arene-exchange mechanism extended to show the various possibilities that might occur. The incoming benzene (pink) can associate with the catalyst at a number of different stages of electronic unsaturation of the catalyst and (partially) hydrogenated benzene (blue) can dissociate at different stages.

The mechanism may be extrapolated to account for arenes which interact with more than one metal centre, possible in a cluster, colloid or nanoparticle, or at a bulk metal surface. The multi-centre coordination modes of arenes have been widely explored and reviewed.¹³ A particularly common coordination mode in cluster chemistry is the $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ mode illustrated in Scheme 2, which has also been recognised on metal surfaces.¹⁴ In the idealised (and observed) system, the Kekulé structure of benzene is realised, with the short double bonds localised over the metal centres.¹⁵ However, a wide range of skewed structures have also been observed by X-ray crystallography (especially for substituted benzenes), although in solution the arene rotates freely¹⁶ and can change coordination mode.¹⁷ By analogy to the arene hydrogenation mechanism described above, the addition of hydrogen across one double bond would result in a $\mu_3\text{-}\eta^2\text{:}\eta^2$ -diene (crystallographically observed for both 1,3-¹⁸ and 1,4-cyclohexadiene¹⁹) and further hydrogenation would lead to a monoene indistinguishable from that in the former mechanism. Arenes can also bridge two metal centres in a $\mu\text{-}\eta^3\text{:}\eta^3$ mode²⁰ and, in principle, a stepwise arene hydrogenation mechanism based on such a bonding mode could be devised.



Scheme 2 The proposed arene-exchange mechanism that could operate at a metal face in a homogeneous cluster or heterogeneous catalyst.

Over the years, the details of the arene-exchange mechanism have changed very little, in stark contrast to the reaction cycles for alkene substrates, where not only elaborate catalyst cycles exist, but the intermediates have also been spectroscopically observed. Despite the lack of direct evidence for the arene-

exchange mechanism, various inferences have been drawn from it and these are used to assess whether arene hydrogenation involves a homogeneous or heterogeneous species. These inferences are analysed below.

Methods used to evaluate the nature of catalysis

A number of chemical and spectroscopic procedures have emerged which help to establish the true nature of catalysis, *viz.* homogeneous *versus* heterogeneous,²¹ and these procedures are summarised below. The first tests that are described can be applied to almost any catalysed reaction, although they are discussed in the context of arene hydrogenations, in which the reductive conditions are ideal for colloid/nanoparticle formation.

The most commonly used method to assess whether a catalyst is homogeneous or heterogeneous is to carry out the reaction in the presence of mercury, which acts as a selective poison towards colloids.²² Typically, the activity of a catalyst is evaluated without mercury present, and then again under identical conditions, except for the presence of mercury. If the activity of the catalyst remains unchanged, then it is most likely homogeneous, but a decrease in activity strongly suggests colloidal/nanoparticle catalysis. Recently, for example, the ruthenium complex, $\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2$ (Cy = cyclohexyl) has been shown to catalyse the hydrogenation of benzene, although turnover frequencies are low [*ca.* $1.6 \text{ mol mol}(\text{cat})^{-1} \text{ h}^{-1}$], under 3 atm of hydrogen at 80 °C.²³ While the catalyst is described as homogeneous, the addition of mercury reduced the activity to zero, suggesting the active catalyst is colloidal. However, there are potential problems with the so-called 'mercury test' that bring its reliability into question. Mercury may react with certain complexes and ligands, deactivating the catalyst, thus reducing the activity. Therefore, when mercury has no effect on the reaction, one can be *certain* that the catalyst is homogeneous, but if the presence of mercury reduces activity, the catalyst is *probably* heterogeneous. Despite this uncertainty, the test remains the most widely used, as it is experimentally very easy to conduct.

In general, the generation of a heterogeneous catalyst from a homogeneous compound is not instantaneous. An incubation period is often observed while the catalyst forms, and before catalysis takes place. Such a process was clearly demonstrated for the $\text{RhCl}_3\text{-Aliquat}^{\text{®}} 336$ catalyst, effective for the hydrogenation of various arenes, including benzene,²⁴ naphthalenes²⁵ and other polyaromatic compounds.²⁶ Originally, this catalyst was presumed to be composed of the solvated ion pair $[(\text{C}_8\text{H}_{17})_3\text{NMe}]^+[\text{RhCl}_4]^-$,²⁷ but a detailed mechanistic study demonstrated that the active catalyst was, in fact, colloidal, with a period of 20–30 min required for catalyst formation.²⁸ However, it is also plausible that certain compounds might additionally undergo a transformation to an active homogeneous catalyst (resulting in a time delay), such as a cluster fragmenting to give an active mononuclear catalyst.

In an extension to the above, should a heterogeneous catalyst form slowly from a homogeneous compound, then it is worth using the catalyst a number of times to see how the activity changes. Dynamic light scattering can provide information on the aggregation process leading to nanoparticulate catalysts derived from homogeneous species, although the technique has not, as yet, been used to probe the nature of arene hydrogenation catalysts. In one well-characterised example, the activity of a fluorinated rhodium catalyst used for the biphasic hydrogenation of terminal alkenes and alkynes was found to increase after each reaction, which is characteristic of colloid formation.²⁹ Colloids were subsequently identified to be the active catalyst using light-scattering experiments and electron microscopy.³⁰ Obtaining images of colloids/nanoparticles is not only helpful in demonstrating their presence, but also for identifying their gross structural features.

Some of the most effective arene hydrogenation catalysts operate in water (see below). For the ruthenium catalyst $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{dppe})\text{Cl}]^+$ [$\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{-ethane}$], the turnover frequency increases with increasing pH, which corresponds to an increase in the amount of nanoparticles produced.³¹ Such a trend (shown in Fig. 1) is characteristic of colloidal catalysis and may be used as an evaluation method.

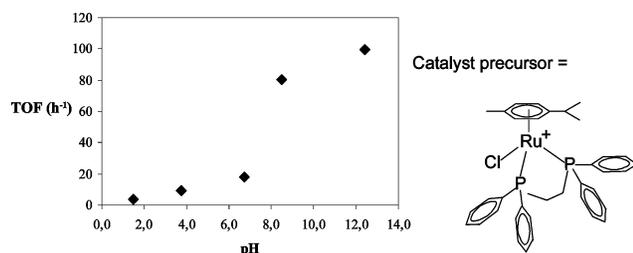
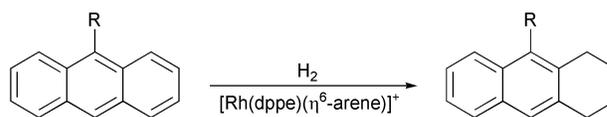


Fig. 1 Effect of pH on the hydrogenation of benzene to cyclohexane using $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{dppe})\text{Cl}]^+$ as the catalyst precursor.

The rigid substrate dibenzocyclooctatetraene coordinates irreversibly to many homogeneous catalysts, and inclusion of this substrate in the catalyst solution should prevent catalysis from taking place if the complex remains in the solution phase.³² For catalytic hydrogenation reactions, including those of arenes, cross-linked polymers functionalised with alkene groups can be used to indicate whether the reaction is catalysed by a homogeneous or heterogeneous catalyst. Apparently, these polymers can only be hydrogenated by homogeneous catalysts.³³ The methods summarised above are used to disprove homogeneous catalysis by showing the presence of heterogeneous catalysts; however, it is generally not considered that a heterogeneous catalyst might react to form a homogeneous catalyst, although this is exactly what takes place in hydroformylation reactions; bulk metals react with H_2 and CO under forcing conditions to form complexes which have been shown to be the active catalysts.³⁴ In addition, a rhodium colloid used to catalyse the Monsanto reaction has been shown to form $[\text{Rh}(\text{CO})_2\text{L}_2]^-$ in significant quantities.³⁵ The general experiments described above are clearly only indicators and specific tests for specific reactions and kinetic studies are essential; the tests available for arene hydrogenation catalysis are reviewed below.

Assuming the arene-exchange mechanism is in operation, then, after reaction, a metal-arene catalyst should have the arene substrate coordinated to it in place of the arene in the starting compound, assuming this is different. A number of papers comment that the original arene in the precursor compound has been replaced by the arene substrate. Perhaps the best characterised example, due to the multiple arene coordination sites in the catalyst, is that of the tetraruthenium cluster $[\text{H}_4\text{Ru}_4(\eta^6\text{-}p\text{-cymene})_4]^{2+}$, which, in the presence of benzene under 60 atm H_2 , heated to 90 °C for 42 h, affords $[\text{H}_4\text{Ru}_4(\eta^6\text{-}p\text{-cymene})_3(\eta^6\text{-C}_6\text{H}_6)]^{2+}$, $[\text{H}_4\text{Ru}_4(\eta^6\text{-}p\text{-cymene})_2(\eta^6\text{-C}_6\text{H}_6)_2]^{2+}$, $[\text{H}_4\text{Ru}_4(\eta^6\text{-}p\text{-cymene})(\eta^6\text{-C}_6\text{H}_6)_3]^{2+}$ and $[\text{H}_4\text{Ru}_4(\eta^6\text{-C}_6\text{H}_6)_4]^{2+}$, as well as related hexahydride derivatives formed by reaction with H_2 .³⁶ Based on the turnover frequency, one would expect to see only the tetrabenzene compounds, unless benzene is hydrogenated at a significantly faster rate than $p\text{-cymene}$. At first glance, it would therefore appear likely that slow arene exchange takes place and the active catalyst is some other species, possibly a heterogeneous catalyst formed under the reaction conditions, but it has been shown that these compounds do not undergo arene substitution under reflux conditions. Complexes of formula $[\text{Rh}(\text{dppe})(\eta^6\text{-arene})]^+$ are reported to catalyse the hydrogenation of anthracenes substituted at the 9-position to 1,2,3,4-tetrahydroanthracenes whilst producing only around 1% of the fully hydrogenated product (Scheme 3).³⁷ Such a reaction could provide evidence for a homogeneous arene-exchange mechanism, but although both



Scheme 3 Hydrogenation of anthracenes substituted at the 9-position to 1,2,3,4-tetrahydroanthracenes catalysed by $[\text{Rh}(\text{dppe})(\eta^6\text{-arene})]^+$ complexes.

electron-donating and -withdrawing substituents were examined, anthracene itself was not studied, which prevents a fuller interpretation of the system as steric hindrance of the substituent could be responsible for the selectivity.

It has been suggested that hydrogenation involving a homogeneous catalyst occurs exclusively on one side of the arene ring. With this hypothesis in mind, a number of papers describe the hydrogenation of C_6D_6 , with analysis of hydrogenation products by NMR spectroscopy. For example, niobium and tantalum arene hydrogenation catalysts have been shown to give the all-*cis* diastereoisomer *cis*- $\text{C}_6\text{H}_6\text{D}_6$, which implies homogeneous catalysis,³⁸ as well as all-*cis* products for various polyaromatic compounds.³⁹ However, the dimer $[\text{Rh}(\text{cod})\text{Cl}]_2$ ($\text{cod} = 1,5\text{-cyclooctadiene}$) acts as a source of colloids for the stereoselective hydrogenation of lignin model compounds,⁴⁰ and classical heterogeneous catalysts such as Raney nickel are also able to give satisfactory *cis* selectivities. The obvious way to interpret this observation is that the arene-exchange mechanism may also operate with colloidal catalysts, and the higher activity of colloidal catalysts could be due to the arene coordinating to more than one metal, as shown in Scheme 2. The structural parameters of face-capping arenes certainly indicate that they are highly activated towards addition, as they tend towards a localised Kekulé structure; however, compared to reactivity studies of $\eta^6\text{-arenes}$, studies on $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-arenes}$ are rare^{13b} and further work is needed before conclusions can be drawn. It has been found that benzene is more prone to the face-capping position than methyl-substituted arenes.⁴¹ One might therefore expect lower rates for the reduction of sterically bulky ligands, which is indeed the case, although this is usually interpreted in terms of electronic effects.

Alternatively, does the colloid release homogeneous (mononuclear) catalysts into solution? A colloidal catalyst prepared from RuCl_3 and tetraalkylammonium salts has been shown to effectively catalyse the hydrogenation of 'milled wood lignin', which has a polymeric structure, albeit poorly defined.⁴² Assuming this is not the case and that stereoselective hydrogenation of arenes can be achieved by colloidal catalysts, then the formation of all-*cis* products cannot be used to confirm homogeneous catalysis. It is also possible that a homogeneous catalyst could give rise to a non-stereoselective hydrogenation product. Considering the final hydrogenolysis step of the arene-exchange mechanism as the η^2 -coordinated cyclohexene transforms to cyclohexane, the η^2 -cyclohexene ring could, in principle, lie almost in a plane perpendicular to that of the arene, possibly allowing addition of hydrogen to either side of the ring. However, in the majority of cyclohexene complexes structurally characterised by X-ray diffraction, the ring lies close to the plane of the original arene, the dihedral angle between the M-C^2 and C^4 planes being typically between 120 and 130°. Only where bulky ligands are present does the cyclohexene lie perpendicular to the original arene ring plane, with the angle approaching 180°.¹²

Assessment of current catalysts that operate in organic solvents

The key arene hydrogenation catalysts that commence with molecular precursors are given in Table 1.

The earliest example of an arene hydrogenation catalyst incorporating rhodium, *viz.* $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$, requires triethylamine to remove HCl generated by the hydrogenolysis of

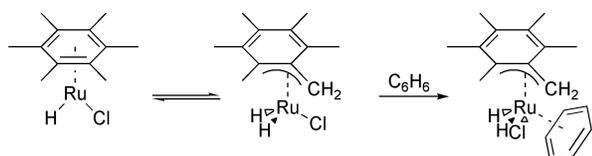
Table 1 Homogeneous, liquid–liquid biphasic and molecular catalysts immobilised on solid supports used in arene hydrogenation; this list is not comprehensive

Catalyst/pre-catalyst	Conditions ^a	Turnover frequency ^b / mol mol(cat) ⁻¹ h ⁻¹	Comment	Ref.
[Rh(η^5 -C ₅ Me ₅)Cl ₂] ₂ + Et ₃ N	Propan-2-ol, 50 atm, 50 °C	~11	Probably heterogeneous	43
Rh(cod)(Ph ₂ PCH ₂ COO)	Neat arene, 5 atm, 50 °C	161 (varies with reaction time)	Probably heterogeneous	44
[Rh(hd)Cl] ₂	Hexane–water, Bu ₄ NHSO ₄ , 1 atm, 25 °C	Lignin model compounds	Probably heterogeneous	69
RhCl{CN(CH ₂) ₃ Si(OC ₂ H ₅) ₃ } ₃ on Ru–SiO ₂	Neat arene, 1 atm, 40 °C	32 (C ₆ H ₅ Me)		88
RhCl{CN(CH ₂) ₃ Si(OC ₂ H ₅) ₃ } ₃ on Pd–SiO ₂	Neat arene, 1 atm, 40 °C	70 (C ₆ H ₅ Me)		88
RhCl{CN(CH ₂) ₃ Si(OC ₂ H ₅) ₃ } ₃ on Pt–SiO ₂	Neat arene, 1 atm, 40 °C	115 (C ₆ H ₅ Me)		88
RhCl(CO){CN(CH ₂) ₃ Si(OC ₂ H ₅) ₃ } ₂ on Pd–SiO ₂	Neat arene, 1 atm, 40 °C	95 (C ₆ H ₅ Me)		88
RhCl{Ph ₂ P(CH ₂) ₃ Si(OC ₂ H ₅) ₃ } on Pd–SiO ₂	Neat arene, 1 atm, 40 °C	28 (C ₆ H ₅ Me)		88
RhCl{Ph ₂ P(CH ₂) ₃ Si(OC ₂ H ₅) ₃ } on Pd–SiO ₂ + O ₂	Neat arene, 1 atm, 40 °C	91 (C ₆ H ₅ Me)		88
[Ru(η^6 -C ₆ H ₆)Cl] ₂	Water, 60 atm, 90 °C	1998		76
Ru(η^6 -C ₆ Me ₆)(PPh ₃)(H)Cl	Not reported, 50 atm, 50 °C	24	Probably heterogeneous	46
[(η^6 -C ₆ Me ₆)Ru(μ -H) ₂ (μ -Cl)Ru(η^6 -C ₆ Me ₆)] ⁺	Propan-2-ol, 50 atm, 50 °C	250		47
Ru(η^6 -C ₆ Me ₆)(η^4 -C ₆ Me ₆)	Neat arene, 3 atm, 90 °C	5	Probably heterogeneous	49
RuH ₂ (H ₂) ₂ (PCy ₃) ₂	Neat arene, 3 atm, 80 °C	1.6	Probably heterogeneous	23
Ru(η^6 - <i>p</i> -cymene)(pta)Cl ₂	Water, 60 atm, 90 °C	170	Possibly heterogeneous	68
Ru(η^6 - <i>p</i> -cymene)(tppts)Cl ₂	Water, 60 atm, 90 °C	488	Heterogeneous	68
[Ru(η^6 - <i>p</i> -cymene)(dippe)Cl] ⁺	Water, 45 atm, 100 °C	18 (pH 6.7)	Heterogeneous	31
[Ru(η^6 - <i>p</i> -cymene)(pta) ₂ Cl] ⁺	Water, 60 atm, 90 °C	150	Probably heterogeneous	68
[Ru(η^6 - <i>p</i> -cymene)(η^2 -triphos)Cl] ⁺	[bmim][BF ₄], 60 atm, 90 °C	476	Possibly heterogeneous	84
[H ₄ Ru ₄ (η^6 -C ₆ H ₆) ₄] ²⁺	Water, 60 atm, 90 °C	269		74
[Ru ₄ (η^6 -C ₆ H ₆) ₄ (OH) ₄] ⁴⁺	Water, 60 atm, 60 °C	606	Partly heterogeneous	71
[Ru ₃ (η^6 -C ₆ Me ₆) ₂ (η^6 -C ₆ H ₆)(μ_3 -O)(μ -H) ₃] ⁺	Water, 60 atm, 110 °C	289		76
[Ru ₃ (η^6 -C ₆ Me ₆) ₂ (η^6 -C ₆ H ₆)(μ_3 -O)(μ -H) ₂ (μ -OH)] ⁺	Water, 60 atm, 110 °C	3644		78
[FeH ₆] ⁻	Neat arene, 3.7 atm, 65 °C	TON 6.6 in 40 h	Rapidly deactivated	50
Co(η^3 -C ₃ H ₅){P(OMe) ₃ } ₃	Neat arene, 1 atm, 25 °C	0.4–0.6	Rapidly deactivated	52
Co(η^3 -C ₃ H ₅){P(O ⁱ Pr) ₃ } ₃	Neat arene, 1 atm, 25 °C	10	Rapidly deactivated	56
Ni(η^6 -C ₆ H ₅ Me)(C ₆ F ₅) ₂	Neat arene, 100 atm, 25 °C	Not reported	Rapidly deactivated	58
Co(η^6 -C ₆ H ₅ Me)(C ₆ F ₅) ₂	Neat arene, 100 atm, r.t.	Not reported		58
Ti(η^6 -C ₆ H ₅ Me)Al ₂ Cl ₈	Neat arene, 1 atm, 125 °C	Not reported	Probably heterogeneous	59
[Nb(OOC ₆ HPh ₄ -2,3,5,6) ₂ Cl ₃] ⁺ + ⁿ BuLi	Neat arene, 82 atm, various temperatures			63
Nb(CH ₂ SiMe ₃)(P ₂ N ₂), ^c R = Cy	Neat arene, 34 atm, r.t.	~10	Rapidly deactivated	66
Nb(CH ₂ SiMe ₃)(P ₂ N ₂), ^c R = Ph	Neat arene, 34 atm, r.t.	~10	Rapidly deactivated	66
Ta(η^2 -C ₄ NMe ₄)(NC ₄ H ₄)Me ₃	Neat arene, 3.5 atm, r.t.	84% conversion in 1 week		67
W(CO) ₃ (MeCN)(tppms) ₂	Water, 82 atm, 140 °C	1.6 (pH > 6), 2.1 (pH < 6)	Heterogeneous at pH < 6	45
Th(C ₅ Me ₅)(CH ₂ C ₆ H ₅) on dehydroxylated γ -Al ₂ O ₃	Neat arene, 13 atm, 90 °C	765		92
Th(CH ₂ C ₆ H ₃ Me ₂ -3,5) ₄ on dehydroxylated γ -Al ₂ O ₃	Neat arene, 13 atm, 90 °C	825		92
Th(η^3 -allyl) ₄ on dehydroxylated γ -Al ₂ O ₃	Neat arene, 13 atm, 90 °C	1970		92

^a Pressure refers to pressure at $t = 0$ s. ^b TOF for benzene, unless otherwise stated. ^c P₂N₂ = RP(CH₂SiMe₂NSiMe₂CH₂)₂PR.

the Rh–Cl bonds.⁴³ Although a high degree of stereoselectivity was observed for the hydrogenation of xylenes, doubts about the homogeneity of the catalyst have been expressed, as it is inactive for the hydrogenation of polymer-bound benzene derivatives.³⁵ Both Rh(cod)(Ph₂PCH₂COO) and Rh(CO)₂(Ph₂PCH₂COO) catalyse the hydrogenation of arenes; however, the turnover frequency depends on the reaction time.⁴⁴ This observation indicates an induction period before the full extent of catalytic activity is realised, which is suggestive of a heterogeneous process.⁴⁵ Furthermore, neither compound shows any stereoselectivity for the hydrogenation of benzene.

The ruthenium complex Ru(η⁶-C₆Me₆)(PPh₃)(H)Cl catalyses the hydrogenation of benzene and it may be reused without any reduction in activity.⁴⁶ It is not easy to speculate on the active species, but the benzene analogue was shown to decompose rapidly in solution, ruling out the arene-exchange mechanism, and heterogeneous catalysis seems most likely. The related dihydrido-bridged ruthenium dimer [(η⁶-C₆Me₆)Ru(μ-H)₂(μ-Cl)Ru(η⁶-C₆Me₆)]⁺ is more active than Ru(η⁶-C₆Me₆)(PPh₃)(H)Cl.⁴⁷ The hydrogenation of C₆D₆ gave a mixture of isomers, indicating that the reaction was not stereoselective. The mechanism for the hydrogenation of arenes has been tentatively proposed to proceed *via* arene exchange and the formation of the proposed active species is shown in Scheme 4.⁴⁸ Although the hexamethylbenzene ligands do not undergo exchange, deuterium incorporation into the coordinated ring is observed, and is accounted for in this mechanism.



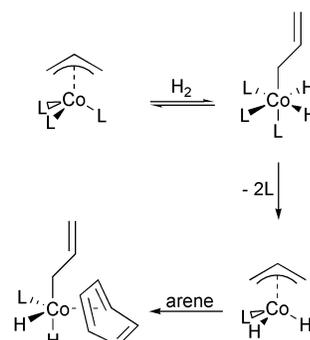
Scheme 4 Proposed activation of [(η⁶-C₆Me₆)Ru(μ-H)₂(μ-Cl)Ru(η⁶-C₆Me₆)]⁺. Slippage of hexamethylbenzene to an η³-allyl bonding mode allows electronic unsaturation and uptake of the arene substrate which could then, in principle, be hydrogenated *via* the arene-exchange mechanism.

A related mechanism was also proposed for the bis-hexamethylbenzene complex Ru(η⁶-C₆Me₆)(η⁴-C₆Me₆).⁴⁹ The turnover frequency for the hydrogenation of benzene was significantly lower than that of the dimer, but was determined under milder conditions. The stereoselectivity was not particularly high for the hydrogenation of xylenes and cyclohexenes were obtained in some quantity from the hydrogenation of benzene. The homoleptic iron hydride complex [FeH₆]⁻ catalyses the hydrogenation of benzene and *p*-xylene, the latter in part to 1,4-dimethylcyclohexene, but decomposition to a rust-coloured precipitate is observed, which indicates colloidal catalysis.⁵⁰

The cobalt complex Co(η³-C₃H₅){P(OMe)₃}₃ catalyses the hydrogenation of benzene under very mild conditions, although the turnover frequencies are low⁵¹ and vary considerably.⁵² This is possibly due to catalyst decomposition that occurs during the reaction which, immediately suggests colloidal catalysis. However, hydrogenation of C₆D₆ affords all-*cis* C₆D₆H₆ in 95% yield.⁵³ Similar stereoselectivity was also found with other substrates, including xylenes and polyaromatics.⁵⁴ It was also observed that the rate of hydrogenation for arenes was similar to the rate for non-aromatic substrates⁵⁵ and, as a result, hydrogenation of substrates with both arene and alkene groups, such as styrene and allylbenzene, gave fully hydrogenated products as well as those in which only the aromatic ring was hydrogenated. Subsequently, related complexes with bulkier phosphite ligands, proved to be more active, with no decrease in selectivity.⁵⁶

The electronically unsaturated compound Co(η³-C₃H₅)H₂L (where L is a phosphine/phosphite ligand) was proposed to be the active catalyst. If hydrogen transfer to the allyl ligand takes place, it results in decomposition *via* hydrogenolysis. However,

coordination of an arene substrate to Co(η³-C₃H₅)H₂L with simultaneous rearrangement of the allyl from η³ to η¹ gives Co(η¹-C₃H₅)(η⁴-arene)H₂L, in which hydrogenation of the free edge of the arene ring can occur (Scheme 5). Next, the usual arene-exchange mechanism takes place to afford cyclohexane. This unusual η⁴ → η²-arene exchange was proposed on the basis of the electronic and coordinative saturation of the proposed intermediates and appears to give the same all-*cis* stereoselectivity that could be achieved with an η⁶ → η⁴ → η² process. Attempts to hydrogenate benzene in the presence of non-conjugated dienes and potential pseudo-dienes gave much lower turnover frequencies. The hydrogenation of a mixture of benzene and allylbenzene, for example, gives no cyclohexane, probably due to the efficient manner in which a non-conjugated pseudo-diene can bond to the catalyst compared to benzene.⁵⁷ Alkene substrates also compete for the catalyst coordination sites and the hydrogenation of mixtures of benzene and 1-hexene gave cyclohexene, cyclohexane and hexane (cyclohexene is not produced in the absence of 1-hexene).



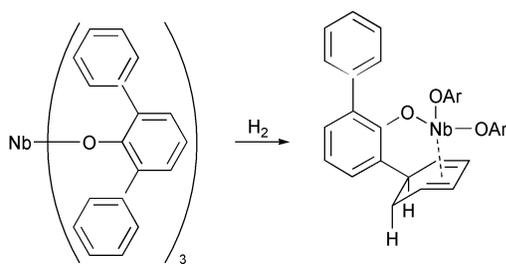
Scheme 5 Formation of the proposed active catalytic species derived from Co(η³-C₃H₅)L₃.

A modified arene-exchange mechanism has been proposed to account for the unusual properties of the cobalt-allyl complex, but ultimately, the destructive hydrogenolysis process limits the turnover number to between 25 and 40. Further limitations are imposed, such as the requirement for a high degree of nucleophilicity from the arene substrate (arenes with electron-withdrawing substituents are not hydrogenated). The complexes are also liable to protonation to give {Co(η³-C₃H₅)HL₃}⁺, which is even more susceptible to hydrogenolysis. Therefore arenes with polar substituents, such as phenol and benzoic acid, deactivate the catalyst. However, both these limitations might also apply to many of the other catalysts described herein; it is just that they have not been tested against such substrates.

The toluene ligand in M(η⁶-C₆H₅Me)(C₆F₅)₂ (where M = Co or Ni) undergoes arene exchange under ambient conditions,⁵⁸ and both compounds also catalyse the hydrogenation of arenes under 100 atm of hydrogen at room temperature. The M-(C₆F₅) bonds undergo hydrogenolysis, leading to metal residues and pentafluorobenzene, and rendering the catalyst inactive. Since the metal residues were found to be catalytically inactive, it would seem that a homogeneous mechanism is in operation, albeit highly unstable. The related titanium complex Ti(η⁶-C₆H₅Me)Al₂Cl₈ catalyses the conversion of benzene to cyclohexane, but turnover frequencies were not reported.⁵⁹ Some decomposition of the titanium complex was observed during the reaction and the possibility that metallic particles are responsible for the catalysis cannot be discounted.

A series of niobium and tantalum compounds with bulky aryloxy ligands were found to catalyse arene hydrogenation following the observation of an intramolecular arene hydrogenation (Scheme 6).⁶⁰

It has been proposed that the electronically unsaturated niobium centre reacts with H₂ to form a dihydride intermediate, Nb(OC₆H₃Ph₂-2,6)₃(H)₂, next the phenyl ring coordinates, and



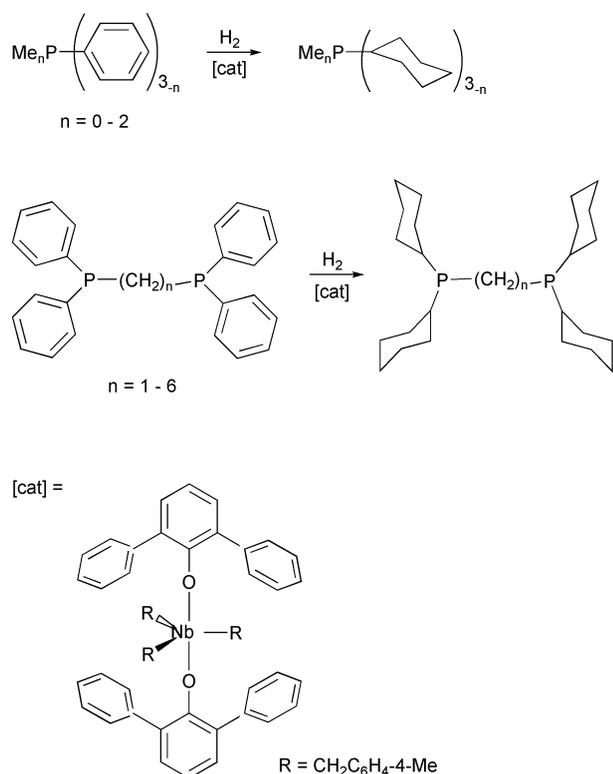
Scheme 6 The intramolecular hydrogenation of the 2-phenyl group of a 2,6-diphenylphenoxide ligand in $\text{Nb}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3$.

is hydrogenated. The 1,2-hydrogenation of the ring occurs exclusively to one side, but the hydrides end up on the opposite face, which presumably occurs through rotation of the ring after hydrogenation. The intramolecular 1,2-hydrogenation of the aryloxy phenyl ring of $\text{Nb}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3$ takes place under mild conditions, whereas further hydrogenation of the aryloxy phenyl rings to give 2,6-dicyclohexylphenoxide groups requires harsher conditions, possibly due to the stability of the quasi- η^4 coordination of the diene ring.⁶¹

To render these compounds catalytically active, a ligand must be included. For example, addition of diphenylmethylphosphine to $\text{Ta}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})(\text{CH}_2\text{SiMe}_3)_3$ under an atmosphere of hydrogen affords $\text{Ta}(\text{OC}_6\text{H}_3\text{Cy}_2\text{-2,6})_3(\text{H})_3(\text{PMe}_2\text{Ph})_2$, which catalyses the stereoselective hydrogenation of benzene and polyaromatic substrates.⁶² Additionally, alkyl niobium and tantalum arene hydrogenation catalysts can be prepared by the *in situ* reaction of $[\text{Nb}(\text{OAr})_3\text{Cl}_2]$ or $[\text{Nb}(\text{OAr})_2\text{Cl}_3]$ and $^n\text{BuLi}$ in the presence of the substrate and hydrogen.⁶³ The active catalyst has not been isolated.

A unique application of the niobium and tantalum catalysts is in the hydrogenation of arylphosphines to give the corresponding cyclohexylphosphines.⁶⁴ Hydrogenation of mono-, bis- and tris-phosphines gives the cyclohexyl products in synthetically useful quantities, as shown in Scheme 7.⁶⁵

These catalysts are unstable towards hydrolysis and the incorporation of $^n\text{BuLi}$ in some of the systems necessitates inert



Scheme 7 Examples of the hydrogenation of arylphosphines to the corresponding cyclohexylphosphines using $\text{Nb}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2(\text{CH}_2\text{-C}_6\text{H}_4\text{-4-Me})_3$.

reactions conditions. However, for air-sensitive substrates like phosphines, such conditions are required anyway.

Under modest pressures of hydrogen, benzene and toluene are hydrogenated in the presence of $\text{Nb}(\text{CH}_2\text{SiMe}_3)(\text{P}_2\text{N}_2)$, $\text{P}_2\text{N}_2 = \text{RP}(\text{CH}_2\text{SiMe}_2\text{NSiMe}_2\text{CH}_2)_2\text{PR}$ and $\text{R} = \text{Cy}$ or Ph .⁶⁶ After catalysis, the alkyl ligand in the original complexes is replaced by an η^5 -cyclohexadienyl ligand derived from the aromatic substrate, although these latter compounds are not catalytically active and the active species remains uncertain. The tantalum complex $\text{Ta}(\eta^5\text{-C}_4\text{NMe}_4)(\text{NC}_4\text{H}_4)\text{Me}_3$ catalyses the conversion of benzene and toluene to cyclohexane and methylcyclohexane, respectively.⁶⁷ When both substrates are present, toluene is hydrogenated in preference to benzene, which contrasts with the normal trend, but is consistent with that of some tethered catalysts described below. No visible precipitate was observed and mercury did not affect the reaction. However, the resonances in the ^1H NMR spectrum corresponding to the tantalum starting material disappear and no new resonances in the normal diamagnetic region of the spectrum are observed, although free tetramethylpyrrole and methane are observed.

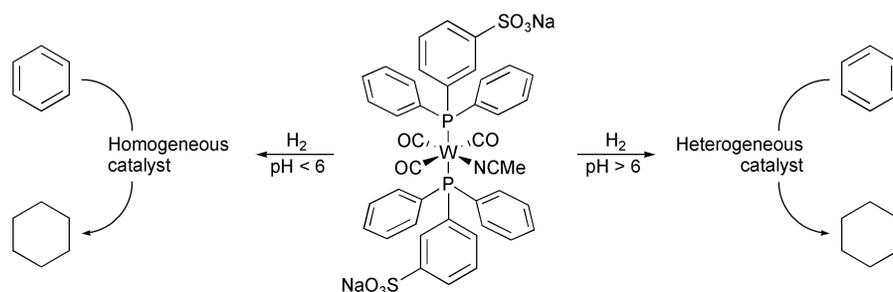
Assessment of catalysts that operate under biphasic conditions

One of the goals in arene hydrogenation catalysis is to produce molecular catalysts that operate in aqueous solution. Despite the problems associated with homogeneous arene catalysts in relatively inert organic solvents, a great deal of effort has been expended in this area and some interesting observations have been made.

The tungsten compound $\text{W}(\text{CO})_3(\text{MeCN})(\text{tppms})_2$ ($\text{tppms} = 3$ -sulfonatophenyldiphenylphosphine sodium salt) catalyses arene hydrogenation in aqueous solution, and the nature of the catalyst varies with pH.⁴⁵ At or below pH 6.0, the activity exhibited is totally suppressed by the addition of mercury, indicative of a heterogeneous catalyst. However, when the reaction is conducted in the presence of an appropriate organic base, both the appearance of the catalytic solution and the turnover frequency for the hydrogenation of benzene differ (see Scheme 8). Significantly, addition of mercury to the basic reaction does not cause a reduction in turnover frequency, indicating a homogeneous process. Since colloids increase with pH, the tungsten catalyst appears to be truly homogeneous. The heterogeneous catalyst appears to be based on tungsten colloids or nanoparticles, but the nature of the homogeneous catalyst is unknown. Nevertheless, the activity of the homogeneous system is low. Degradation of the catalyst also appeared to occur in both the homogeneous and heterogeneous modes of operation.

The ruthenium complexes $\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{pta})\text{Cl}_2$ ($\text{pta} = 1,3,5$ -triazad-7-phosphaadamantane), $\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{tppts})\text{-Cl}_2$ ($\text{tppts} = \text{tris-3-sulfonatophenylphosphine trisodium salt}$) and $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{pta})_2\text{Cl}]^+$ catalyse the hydrogenation of benzene and other arenes under aqueous-organic biphasic conditions.⁶⁸ The active catalysts are believed to be very different. The pta compound $\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{pta})\text{Cl}_2$ is converted into a (homogeneous) trinuclear cluster, which is the proposed catalyst (see below). The mono- tppts complex converts to a colloid under the reaction conditions, while the cation $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{pta})_2\text{Cl}]^+$ is thought to act as a mononuclear homogeneous catalyst. The main evidence for homogeneous catalysis was provided by identification of the exchanged arene complex after reaction; however, as mentioned above, such indirect evidence is not sufficient to completely rule out colloidal catalysis and further characterisation is required, especially since the closely related complex $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{dppe})\text{Cl}]^+$ has been shown to be a precursor to a colloidal catalyst under similar conditions.³¹

The dimer $[\text{Rh}(\eta^4\text{-hd})\text{Cl}]_2$ ($\text{hd} = 1,5$ -hexadiene) combined with tetrabutylammonium hydrogen sulfate in a phase-transfer



Scheme 8 pH-dependent homogeneous/heterogeneous hybrid catalysis resulting from the pre-catalyst $W(CO)_3(MeCN)(tppms)_2$.

system catalyses the hydrogenation of benzene.⁶⁹ Under very mild conditions, the turnover frequencies are apparently high. The stereoselectivity of the catalyst was demonstrated in the hydrogenation of naphthalene and *p*-methylanisole, which yielded all-*cis* products. However, the homogeneity of this catalyst is in some doubt, as the same dimer has been used for the hydrogenation of lignin model compounds and colloids were shown to be the active catalysts.⁷⁰ In fact, it would seem likely that all phase-transfer systems used for arene hydrogenation result in colloidal catalysts and that organometallic compounds with labile ligands are among the best colloidal precursors.⁸

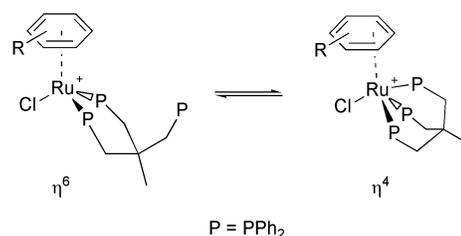
The ruthenium cubane cluster $[Ru_4(\eta^6-C_6H_6)_4(OH)_4]^{4+}$ exists as a tetramer in aqueous solution and is a pre-catalyst for arene hydrogenation.⁷¹ After catalysis, the electronically unsaturated dimer $[Ru_2(\eta^6-C_6H_6)_2(\mu-OH)_2]^{2+}$ is the main species present and it has been proposed to be the active catalyst. Hydrogenation of benzene in the presence of mercury reduces the turnover frequency by *ca.* 20%, showing that at least some of the initial activity is colloidal.

The discovery that a tetraruthenium cluster, $[H_4Ru_4(\eta^6-C_6H_6)_4]^{2+}$, catalysed the hydrogenation of fumaric acid⁷² led to the development of a series of cluster catalysts. Under an atmosphere of hydrogen, $[H_4Ru_4(\eta^6-arene)_4]^{2+}$ reacts to form $[H_4Ru_4(\eta^6-arene)_4(H_2)]^{2+}$, which has been proposed to be the active catalyst.⁷³ The catalytic turnover frequencies for the biphasic hydrogenation of benzene is considerably higher than most mononuclear compounds.⁷⁴ The all-*cis* isomer of C_6D_6 was recovered as the only product of the hydrogenation of C_6D_6 . The hydrogenation of styrene gives a mixture of ethylbenzene and ethylcyclohexane, and the hydrogenation of allylbenzene affords propylbenzene and methylstyrene isomerisation products. Although the tetraruthenium clusters were originally thought to be the active hydrogenation catalysts, there is some doubt as to their precise involvement as a result of the observation that the parent dimer of both these clusters is more active.⁷⁵ The clusters are prepared by the reaction of aqueous solutions of $[Ru(\eta^6-arene)Cl_2]_2$ under 1 atm of hydrogen. However, when the high pressure reaction was conducted in the presence of an excess of arene, hydrogenation occurred with a turnover frequency of 1998 mol mol(cat)⁻¹ h⁻¹, considerably higher than that of the clusters, and symptomatic of colloidal catalysis. The dimer had, in fact, been previously reported as an active arene hydrogenation catalyst,⁷⁶ but the only species recovered from the reaction were the tetraruthenium clusters, raising the possibility that a more active intermediate species is involved. A new species characterised as $[Ru_3(\eta^6-C_6H_6)_3(\mu-Cl)(\mu_3-O)(\mu-H)]^+$ was detected, but under high pressures of hydrogen it is converted to the tetraruthenium cluster. The bis-hexamethylbenzene analogue $[Ru_3(\eta^6-C_6Me_6)_2(\eta^6-C_6H_6)(\mu_3-O)(\mu-H)_3]^+$ was found to be less active for the hydrogenation of benzene than $[H_4Ru_4(\eta^6-C_6H_6)_4]^{2+}$, but, remarkably, more active for the hydrogenation of toluene and ethylbenzene. Analysis of the catalyst after hydrogenation showed that a further species, $[Ru_3(\eta^6-C_6Me_6)_2(\eta^6-C_6H_6)(\mu_3-O)(\mu-H)_2(\mu-OH)]^+$, formed.⁷⁷ This new compound is highly active for the hydrogenation of benzene, giving a turnover

frequency of 3644 mol mol(cat)⁻¹ h⁻¹.⁷⁸ The high activity led to the proposition of a new mechanism for arene hydrogenation catalysis, termed supramolecular catalysis, as arene exchange does not appear to take place and there is convincing evidence that arenes can associate with the cluster face without covalently binding. Partial and reversible slippage of hexamethylbenzene could also provide a route for the coordination of arenes instead of a supramolecular mechanism, but hydrogenation is not stereoselective and, in addition, 1,3-cyclohexadiene and cyclohexene are formed in low quantities.

Ionic liquids provide a polar, non-nucleophilic environment which can increase catalyst lifetimes in certain biphasic processes.⁷⁹ Such an observation is important, as biphasic catalysis has been criticised since homogeneous catalyst lifetimes are often short making it arguably not worth finding ways to recycle and reuse them.⁸⁰ A few arene hydrogenation catalysts have been screened in ionic liquids, generally charged ones, as these tend to be highly soluble and well retained in the ionic liquid during product separation.⁸¹ The cubane $[Ru_4(\eta^6-C_6H_6)_4(OH)_4]^{4+}$ is almost inactive in the ionic liquid [bmim][BF₄] (bmim = 1-butyl-3-methylimidazolium cation), presumably due to activation by water when used in aqueous media, whereas the cluster $[H_4Ru_4(\eta^6-C_6H_6)_4]^{2+}$ is slightly more active than when used in a water biphasic.⁸² It was found that the purity of the ionic liquid was critical, with chloride impurities impeding activity.⁸³

A ruthenium-1,1,1-tris(diphenylphosphinomethyl)ethane (triphos)-based compound, $[Ru(\eta^6-p-cymene)(\eta^2-triphos)Cl]^+$, with similarities to the cobalt-allyl catalyst described above, has been evaluated in dichloromethane under homogeneous conditions and in [bmim][BF₄] ionic liquid.⁸⁴ Essentially, in dichloromethane, activity is much lower than in the ionic liquid and deactivation takes place. In contrast, the catalyst operates in the ionic liquid with no observable decrease in activity. The catalyst cannot be extracted from the ionic liquid, but can be detected by mass spectrometry.⁸⁵ The similarity to the cobalt-allyl catalyst derives from it being more active towards arenes than alkenes, and a similar modified arene-exchange mechanism to that proposed for the cobalt compound can also be invoked; *viz.* the free phosphine assists by reversible coordination to the ruthenium involving an 'arm-on/off' mechanism. This could have the effect of causing the ring to slip from the η^6 to the η^4 mode, thereby promoting hydrogenation of the uncoordinated arene edge (see Scheme 9).



Scheme 9 Proposed mechanism for activation of the coordinated arene towards hydrogenation in $[Ru(\eta^6-p-cymene)(\eta^2-triphos)Cl]^+$.

Mercury does not affect the activity and hydrogenation of C_6D_6 affords only a single isomer of $C_6D_6H_6$. Substrates such as styrene and divinylbenzene are resistant to hydrogenation and it has been proposed that they form an η^4 interaction *via* the vinyl double bond and the arene which inhibits hydrogenation. However, since $[Ru(\eta^6-p\text{-cymene})(dpe)Cl]^+$ has been shown to be a precursor to a colloidal catalyst, it is possible that activity is also heterogeneous. A related ruthenium–triphos compound has been tethered to a silica support and shown to hydrogenate heteroaromatics and polyaromatics.⁸⁶ Other alternative solvents, such as fluorinated solvents and supercritical fluids, have not been used to immobilise arene hydrogenation catalysts. However, the solubility of cyclohexane products in ionic liquids is generally lower than the arene substrates, which leads to high reaction rates not limited by mass transport, combined with excellent separation, making them the solvent of choice.

Molecular catalysts immobilised on solid supports

A number of molecular compounds tethered to solid supports catalyse arene hydrogenation reactions. With all these systems, it is very difficult to assess whether the tethered compound remains as a discrete molecular species, or whether they react to form nanoparticles. However, there are some parallels between these systems and those described above which make them relevant to the discussion.

Simple silica and alumina supports have been used to immobilise a range of different complexes, resulting in active arene hydrogenation catalysts. For example, rhodium, niobium, tantalum and Group 4 complexes hydrogenate benzene, xylenes and naphthalene.⁸⁷ Perhaps the most interesting support materials contain metal nanoparticles, in what are termed a tethered catalyst on supported metal (TCSM).⁸⁸

TCSM systems based on $RhClR_3$ and $RhCl(CO)R_2$, $R = \{CN(CH_2)_3Si(OC_2H_5)_3\}$, supported on 10% w/w Pd– SiO_2 catalyse arene hydrogenation under mild conditions (Fig. 2).⁸⁸ The two rhodium complexes are inactive under homogeneous conditions and also when supported on SiO_2 alone, and the Pd– SiO_2 support exhibits much lower activity on its own. These observations indicate synergistic interactions between the supported metal and the tethered complex.

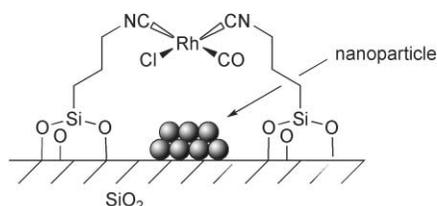


Fig. 2 Representation of $RhCl(CO)R_2$, $R = \{CN(CH_2)_3Si(OC_2H_5)_3\}$, supported on 10% w/w Pd– SiO_2 .

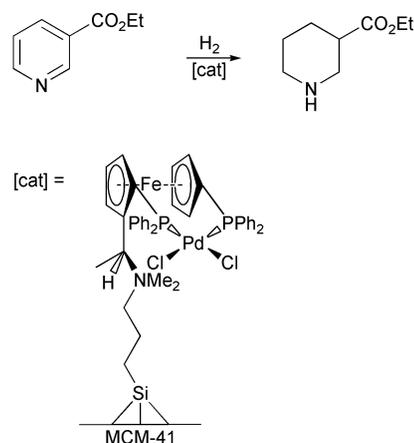
Silica impregnated with platinum, with the same tethered complexes, gives higher turnover frequencies under the same conditions,⁸⁹ whereas impregnation with ruthenium leads to lower reaction rates. However, the turnover frequencies of all the catalysts decrease after 15–20 h, due to particle aggregation arising from eddy effects rather than deactivation, and re-dispersion of the catalysts restores activity. Diffuse reflectance infrared fourier transform (DRIFT) spectroscopy showed that the tethered complexes are almost identical in nature to the free complexes. After reaction, the $RhClR_3$ species is unchanged, whereas the carbonyl is no longer present in $RuCl(CO)R_2$, but, in both cases, the rhodium–isonitrile bond remains intact.

Modified phosphine ligands have also been used to tether complexes to solid supports, and $RhCl\{(Ph_2P(CH_2)_3Si(OC_2H_5)_3)\}$ tethered to silica impregnated with nickel, palladium or gold leads to active arene hydrogenation catalysts.⁹⁰ The palladium-containing support is far superior to the others,

and since palladium is known to absorb high concentrations of hydrogen, it is possible that the palladium provides the molecular complex with hydrides in what has been termed a ‘spillover process’. Again, all the TCSM catalyst–support combinations are more active than their separate components. Unusually, prolonged exposure of the $RhCl\{(Ph_2P(CH_2)_3Si(OC_2H_5)_3)\}/Pd-SiO_2$ catalyst to air before use led to increased turnover frequencies. DRIFT and solid state ^{31}P NMR analysis indicated that the active species in the air-exposed catalyst contained an oxidised phosphine species, which increases the activity.

The catalysts $RhCl(CO)_2\{Et_2N(CH_2)_3Si(OC_2H_5)_3\}$, $RhCl(CO)_2\{H_2N(CH_2)_3Si(OC_2H_5)_3\}$ and $RhCl(cod)\{H_2NCH_2CH_2NH(CH_2)_3Si(OC_2H_5)_3\}$, containing modified amines, have been immobilised on silica impregnated with nickel, palladium or gold.⁹¹ Of the three catalysts, the hydrogenation of toluene is effected most successfully by $RhCl(CO)_2\{Et_2N(CH_2)_3Si(OC_2H_5)_3\}$ on Pd– SiO_2 . This catalyst is also active for the hydrogenation of benzene, but, unlike other catalysts, which generally exhibit higher turnover frequencies for the hydrogenation of benzene relative to toluene, the reverse trend is observed here. Again, exposure of the $RhCl(CO)_2\{Et_2N(CH_2)_3Si(OC_2H_5)_3\}/Pd-SiO_2$ TCSM catalyst to air results in an improvement in activity, with the turnover frequency for the hydrogenation of toluene being almost doubled. In this instance, DRIFT spectroscopy showed that exposure to air had facilitated the displacement of the carbonyl ligands, yielding a more active catalyst.

Supported metal catalysts incorporating metals not employed in the homogeneous systems described in the previous sections have also been evaluated in arene hydrogenation. For example, $Th(C_5Me_5)(CH_2C_6H_5)$, $Th(CH_2C_6H_3-3,5-Me_2)_4$ and $Th(\eta^3\text{-allyl})_4$ supported on dehydroxylated γ -alumina catalyse the hydrogenation of benzene under relatively mild conditions.⁹² Arene exchange at the thorium centre is proposed, although the hydrogenation of C_6D_6 gave a 3 : 1 mixture of the possible isomers. Zirconia complexes on super-acidic supports also show promising activity as arene hydrogenation catalysts.⁹³ The MCM-41-supported palladium complex shown in Scheme 10 effectively catalyses the hydrogenation of heteroaromatics.⁹⁴ However, heteroaromatics, like polyaromatics, are considerably easier to hydrogenate than C_6 arenes, and many related examples are known.



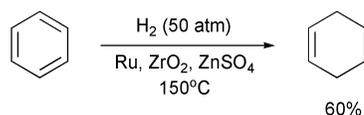
Scheme 10 Hydrogenation of a functionalised heteroaromatic using a chiral palladium complex supported on MCM-41.

Partial hydrogenation of arenes

Although reduction of arenes to their corresponding cyclohexanes is important, partial reduction to cyclic dienes or monoenes also represents a synthetically useful reaction, and is most frequently conducted with stoichiometric reagents, notably the Birch reduction, but progress has also been made with catalytic transformations.⁹⁵ The main obstacle to overcome in

the catalytic partial reduction of arenes is that once the aromaticity is broken, the remaining bonds are reduced much more easily and preferentially. In addition, elimination of a diene, either coordinated or chemisorbed, is difficult as they bind strongly to the metal(s), whereas cyclohexenes are more easily released (and are sometimes observed fortuitously, whereas cyclohexadienes tend not to be observed).⁹⁶

The most effective catalyst for the conversion of benzene to cyclohexene (Scheme 11) is used on an industrial scale and employs a selective bilayer catalytic system including a ruthenium metal catalyst, ZrO₂ and ZnSO₄. The process affords cyclohexene with 60% selectivity after 90% conversion of benzene, and, presently, it produces 50 000 tons of cyclohexene per year, which are converted into 60 000 tons of cyclohexanol.⁹⁷



Scheme 11 The Asahi Chemical Co. process for regioselective hydrogenation of benzene.

Catalysts that operate in solution (whether homogeneous or not) tend to give cyclohexenes as minor products. As in stoichiometric reactions, the double bond may be stabilised by a substituent group. For example, [FeH₆]⁻ catalyses the hydrogenation of benzene to cyclohexane only, whereas 1,4-dimethylcyclohexene is isolated together with the full hydrogenated product from the reduction of *p*-xylene.⁵⁰ A poly-oxoanion-stabilised Rh(0) nanocluster catalyses the partial reduction of anisole to 1-methoxycyclohexene with a yield of 8%.⁹⁸ It would appear that the isolation of cyclic dienes has only been observed with the cluster [Ru₃(η⁶-C₆Me₆)₂(η⁶-C₆H₆)(μ₃-O)(μ-H)₂(μ-OH)]⁺, in which small quantities of 1,3-cyclohexadiene are observed in the hydrogenation of benzene.⁷⁸ This observation points towards the proposed supramolecular mechanism, or at least a somewhat weaker interaction in order to release the diene. The formation of 1,4-dienes has not been observed and would require an additional isomerisation step or a different hydrogenation path to the arene-exchange mechanism.

Effect of solvent

Solvent is known to have a dramatic effect on many catalysts, changing the selectivity and rate of a reaction, and causing catalyst deactivation. It is possible that the same molecular complex could catalyse a reaction as a homogeneous species in one solvent, while forming a heterogeneous catalyst in another. For example, W(CO)₃(MeCN)(tppms)₂ catalyses arene hydrogenation in aqueous solution, at high pH the catalyst is believed to be homogeneous and at low pH heterogeneous.⁴⁵ Unfortunately, arene hydrogenation catalysts that appear to be homogeneous have not been studied in different solvents.

An interesting area worth comparing with the homogeneous *versus* heterogeneous debate in arene hydrogenation is that of molecular cluster catalysis. For many years, the concept of intact cluster catalysis in solution was contested, despite some convincing examples of heteronuclear systems which exhibited properties that suggested a synergy between the different metals.⁹⁹ Direct evidence was not forthcoming and an increasing number of reactions thought to be catalysed by intact clusters were later found to be catalysed by mononuclear fragments. The rules used to distinguish cluster catalysis, much like those used to assess arene hydrogenation catalysts, seemed flawed. However, very recently, the first direct evidence for intact cluster catalysis was provided by parahydrogen NMR spectroscopy.¹⁰⁰ Subsequently, it was found that solvent plays a critical role, with

non-polar solvents resulting in catalysis by cluster fragments.¹⁰¹ Such solvent effects were clearly responsible for some of the confusion, and it would be interesting to see if solvent can determine the nature of the catalyst in the hydrogenation of arenes. Ionic liquids may have a role to play as they are polar, but not non-nucleophilic, and might therefore stabilise a homogeneous arene hydrogenation catalyst. Solvent could also play a determining role in regioselective hydrogenation of arenes.

Concluding remarks

Many so-called homogeneous catalysts would appear to be pre-catalysts to heterogeneous catalysts and, in general, the more tests that an arene hydrogenation catalyst is subjected to, the greater the chance that it is found to be heterogeneous. Unfortunately, not all the methods used to evaluate homogeneous arene hydrogenation catalysis stand up to scrutiny, which complicates the area somewhat. Some catalysts certainly appear to be homogeneous, for example, the niobium and tantalum catalysts with aryloxy ligands and the cobalt catalysts with allyl ligands, but, in general, turnover frequencies and numbers are low, and such activity might be typical of homogeneous arene hydrogenation catalysts. It seems likely that many catalysts commence as homogeneous but rapidly decompose to give heterogeneous catalysts. Turnover frequencies of adventitiously formed nanoparticulate catalysts are generally higher than those which seem to correspond to homogeneous catalysts and tend to be similar to specifically designed nanoparticulate catalysts. It would also appear that both homogeneous and heterogeneous catalysis can take place simultaneously, which further complicates matters. Careful selection of solvent may help to determine which type of catalyst will dominate, but, ultimately, direct experimental evidence for homogeneous arene reduction would be very welcome.

Acknowledgements

I would like to thank the Royal Society (London), the Engineering and Physical Sciences Research Council (UK) and ICI who originally supported my work in this field. Since moving to Switzerland, I am grateful to the Swiss National Science Foundation, the EPFL, Novartis and the Roche Research Foundation for funding my research.

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